

In the last column, UL, the values of V_c are given, calculated by the same formula, but using for P the temperature variation deduced from the experiments on the upper limit. The correspondence of columns 4 and 5, and the divergence in column 6, are quite sufficient to show that the temperature variation of the lower limit is in agreement with the law of viscosity rather than with the formula obtained from the upper limit. The experiments are important in showing a close agreement with the theoretical formula of Reynolds, which requires not only the viscosity formula to hold, but the inverse-diameter law as well. The agreement of the individual observations confirms our previous conclusions, in showing the uncertainty in measuring critical velocity, not from the want of accuracy in the measuring appliances, but from the variation in the point itself. It is only by taking a mean of a number of observations that anything like an accurate value can be obtained.

"The *Rôle* of Diffusion during Catalysis by Colloidal Metals and Similar Substances." By HENRY J. S. SAND, Ph.D., M.Sc., University College, Nottingham. Communicated by Professor J. H. POYNTING, F.R.S. Received November 22,—Read December 8, 1904.

In a paper on reaction-velocities in heterogeneous systems, Nernst* has recently put forward the view that all chemical reactions taking place on the boundary of two phases proceed to equilibrium practically instantaneously, and that the velocities actually observed are simply those with which diffusion and convection renew the reacting material at the boundary. As a special instance of heterogeneous reactions, he mentions catalytic decompositions due to finely divided particles, such as colloidal metals, and he believes it probable that the kinetics of these reactions can be deduced from the assumption that chemical equilibrium remains permanently established on the surface of the particles.

Processes of this kind have recently undergone a considerable amount of experimental investigation, the most important instances being the catalytic decomposition of hydrogen peroxide due to colloidal platinum† and colloidal gold‡ by Bredig and his pupils, and the catalytic decomposition of the same substance due to hæmase by Senter.§ In his last paper Senter discusses his reaction in the light of Nernst's hypothesis, and arrives at the conclusion that the known facts do not contradict it.

* 'Ztschft. Phys. Chem.,' vol. 47, p. 52 (1904).

† Bredig and Müller, v. Berneck, 'Ztschft. Phys. Chem.,' vol. 31, p. 258 (1899); Bredig and Ikeda, *ibid.*, vol. 37, p. 1 (1901).

‡ Bredig and Reinders, 'Ztschft. Phys. Chem.,' vol. 37, p. 323 (1901).

§ *Ibid.*, vol. 44, p. 257 (1903); 'Roy. Soc. Proc.,' vol. 74, p. 201 (1904).

With regard to this result, it must be observed that a colloidal solution of hæmase does not afford the most suitable example from which to draw theoretical conclusions, as nothing whatever is known regarding the size of the active particles, their nature and their number. More definite results can be obtained from a criticism of Bredig's experiments, for in them we are dealing with platinum, or gold, substances of known properties, the absolute quantities of which are stated for every experiment. Moreover, although we are without definite information regarding the shape, size, and number of the particles, yet we are safe in assuming that in those colloidal solutions which were at all stable, no particles occurred of a diameter greater than 0.5μ .^{*} In order to carry out any calculations, the diffusion coefficient of hydrogen peroxide is also requisite. So far as I am aware, this number has not been determined. If we take as representative of diffusion coefficients of non-electrolytes at 25° , the following values determined by Scheffer for molecules heavier than that of hydrogen peroxide:—

Urea, $0.94 [1 + (25^\circ - 7.5^\circ) 0.025] 10^{-5} = 1.35 \times 10^{-5} \text{ cm}^2/\text{sec.}$;

Chloral hydrate, $0.64 [1 + (25^\circ - 9^\circ) 0.025] 10^{-5} = 0.86 \times 10^{-5} \text{ cm}^2/\text{sec.}$;

Mannite, $0.44 [1 + (25^\circ - 10^\circ) 0.025] = 0.60 \times 10^{-5} \text{ cm}^2/\text{sec.}$,

we see that we shall probably not make a very large error, and not take a too high value, if we assume for hydrogen peroxide a diffusion coefficient of $10^{-5} \text{ cm}^2/\text{sec.}$

Summary of the Available Experimental Results.—It will be convenient to preface this discussion by a summary of the available results.

In neutral and acid solutions Bredig found that the reaction proceeded as one of the first order, that is, it was expressed by the equation

$$\frac{1}{t} \log \frac{C_0}{C} = K \dots \dots \dots (1),$$

in which C_0 is the initial concentration of the hydrogen peroxide, C its concentration after the time t , and K a constant. The same equation holds for hæmase, according to Senter's experiments. In alkaline solution, no general formula was found by Bredig to express the results. The constant K is greatly influenced by the addition of certain substances (poisons) ; it varies more rapidly than proportionally with the concentration of the catalyser, and increases geometrically with change of temperature, rising to its threefold value every 20° .

On the Relative Size and Available Surface of the Particles in Wholly and Partially Poisoned Solutions.—I do not propose to enter into a discussion of the effect of poisons more deeply than is required for the primary objects of the present paper. It seems that two explanations are compatible with Nernst's views. Firstly, in the case of substances

^{*} *Loc. cit.*, vol. 31, p. 272.

which have a very powerful effect, an inactive film may be formed on the particles by chemical action of the poison, whenever the concentration of the latter in the solution is greater than a certain definite value, and the platinum would thus be completely poisoned as soon as this value was exceeded by the small quantity necessary to form the coating. Such an explanation is, however, manifestly not applicable to weak poisons, such as acids and certain electrolytes, the action of which begins at low concentrations, and is not complete until very large values are attained. In this case it seems that the only explanation compatible with Nernst's hypothesis would have to be sought in the tendency of such substances to cause the coalescence and final precipitation of the particles. The influence of alkalis in accelerating the reaction would lie in their tendency to bring about further disintegration of particles which had already undergone partial coalescence.* In any case, however, as has already been pointed out, we may assume that in solutions which are at all stable no particles occur of a diameter greater than 0.5μ .

The Experimental Results on Dependence of Reaction Velocity on Concentration of the Catalyser can only be Reconciled with the Idea of a Heterogeneous Reaction by Recognising the Important Part Played by Convection Currents.—It is *a priori* clear with regard to the relative rôle of diffusion and convection that the latter must be seriously considered, owing to the fact that solid particles suspended in a liquid are known to be in a state of continual movement performing the so-called Brownian motions. Besides, in the more concentrated solutions oxygen-bubbles are given off, and cannot fail to stir the liquid.

As a matter of fact, a brief examination of the results summarised above suffices to show that they are not in agreement with Nernst's hypothesis, if we suppose diffusion alone, without convection, to be responsible for the neutralisation of changes of concentration. We may even go further, and say that the fact that K increases more rapidly than proportionally with the concentration of the catalyser cannot be reconciled with the idea of a heterogeneous reaction at all, unless the process taking place on the surface of one of the particles influences that of its neighbours by some non-chemical means, such as the production of convection currents. If we were dealing with a stationary liquid, whatever the chemical mechanism of the reaction may be, the amount of substance decomposed in a given time at the beginning of the experiment would be proportional to the number of particles, that is, to the concentration of the platinum. Now, the constant K may be taken as a direct measure for this amount, as is clear from the following relation arising from Equation 1,

$$-\frac{dC}{dt} = CK \dots \dots \dots (2).$$

* Bredig, *loc. cit.*, vol. 31, p. 306, note 2.

Bredig's results thus contradict the idea of a heterogeneous reaction taking place in a stationary liquid. They, however, become intelligible if we consider the influence of convection. Proceeding on lines similar to those adopted by Nernst, we may assume each particle to be surrounded by a film of adhering liquid, the thickness of which depends very largely on the amount of motion taking place in the solution. The thinner the film, the greater will be the flow of solute to the particles, and the greater, therefore, the velocity of the reaction. Now, in the solutions containing large quantities of the catalyser, considerably more convection is produced than in those in which small quantities are present, owing to the brisker evolution of bubbles of oxygen gas, and in this fact the explanation of Bredig's result is very probably to be sought.

In accordance herewith, we should expect that in solutions containing very small amounts of catalyser, and in which, consequently, the evolution of oxygen is so slight that no gas-bubbles are produced, no deviation from the law of proportionality between K and the concentration of the catalytic particles would occur.

This point has not been specially tested by Bredig, but by collating results scattered over his paper, we may gather that the conclusion drawn is correct. Thus, in Table 11, first part, p. 291, we have for a concentration of $N/30000$ platinum an average value of K of approximately 0.016 min.^{-1} , whereas, at the end of Table 13, p. 300, we have, at a later date, with the same platinum solution, diluted to a concentration of $N/300000$ K , approximately equal to 0.0012 min.^{-1} , i.e., only slightly less than one-tenth of the former value.

In agreement with this, Senter found that in his very dilute solutions the velocity of the reaction was proportional to the concentration of the catalyser, whereas in more concentrated solution it increased more rapidly.

The Experimental Results on Dependence of Reaction Velocity on Temperature Cannot be Reconciled with Nernst's Hypothesis unless Convection Plays an Important Part.—Bredig's results regarding the influence of temperature cannot be reconciled with Nernst's hypothesis if we suppose the particles and liquid to be stationary. In this case the only effect of a rise of temperature would be to increase the diffusion coefficient of the solute by about $2\frac{1}{2}$ per cent. per degree, and the result of doing this can be seen from the following theorem:—If concentrations in a liquid are determined solely by diffusion according to Fick's law, in such a manner that they arise out of a given initial state and a condition not defined as a time-relation which is maintained uniformly throughout the experiment (such as the one that the concentration is permanently kept at zero on the surface of stationary particles of any shape and distribution whatever), then the concentration at any point may be expressed as a function only of the co-ordinates of that point

and the product of the diffusion coefficient and the time, the average concentration being a function only of the product of the diffusion coefficient and the time.*

By the application of this theorem to Equation 1, we find that if this equation were the result solely of diffusion in a stationary liquid, then in order that it may conform with Nernst's hypothesis, the constant K must increase by about $2\frac{1}{2}$ per cent. per degree. This is a far smaller increase than that actually observed. If, however, convection takes place with increasing efficiency as the temperature rises, there is so far no contradiction with Nernst's hypothesis.

If the Distribution of the Particles is Fine Enough, the Concentration Throughout the Liquid will be Practically Uniform.—It should be pointed out here that if only the disintegration of the particles is great enough and their distribution consequently fine enough, changes of concentration occurring on their surfaces will be transmitted practically instantaneously throughout the liquid by diffusion. In this case, if Nernst's hypothesis is correct, the concentration of the whole solution would be instantaneously reduced to zero, but even if this hypothesis does not hold, the idea of a heterogeneous reaction would demand that the velocity of reaction at a given concentration of the solute should be proportional to the concentration of the catalysing particles.

If Nernst's Hypothesis Holds, the Reaction Velocities Found by Bredig must be Greater than those Calculated for a Stationary Liquid.—We have thus seen that convection currents play an important part in the processes under discussion, and always tend to accelerate them. The last-named fact opens up a way by means of which to apply a direct test to Nernst's hypothesis. If, on this hypothesis, an expression could be calculated which is equal to or smaller than the reaction velocity under the smallest conceivable amount of convection, this expression should always be smaller than the experimentally found values, and if it is equal to or greater than the latter, this would prove that Nernst's hypothesis must be discarded in the cases under investigation, *i.e.*, that the concentration of hydrogen peroxide on the surfaces of the particles is not permanently maintained at zero.

As has already been stated, we possess an upper limit for the diameter of the particles, and we shall assume them all to be spheres of this diameter, thus being certain to obtain a minimum value for

* There is no difficulty whatever in proving this theorem in a purely mathematical way, but it becomes immediately obvious, when we remember that we can give the diffusion coefficient κ any desired value $\alpha\kappa$ by increasing the unit of time to its α -fold value. In the new units any interval of time which before was expressed by t is now given by t/α , and in order that concentrations after any real interval of time may remain unaltered, the above theorem must hold.

reaction velocity. It is evident that if a given volume were distributed in pieces of larger surface and more especially in flat pieces or in pieces of smaller diameter, a much larger reaction velocity would arise.

We again assume each particle to be surrounded by an adhering film of liquid, in which no convection occurs, in such a manner that the greater the amount of stirring or motion in the solution, the smaller the thickness of this layer. On the outside of the film the concentration may be considered to have a definite value which is not exceeded in any part of the solution. If the film is exceedingly thin, then the flow of solute to the particle will continually be very great and roughly inversely proportional to the thickness of the film. If the latter, however, be thick, then, as will be seen in the sequel, the flow of solute to the particle rapidly decreases to a value corresponding to a permanent distribution of concentration in such a manner that this flow becomes practically independent of the thickness of the layer and only depends on the concentration outside.

It should be pointed out here that a limit is set to the thickness of the films by the fact that their total volume must be smaller than that of the liquid. If each layer with its enclosed particle forms a sphere of radius R , and N is the number of particles per unit volume, we, therefore, have the inequality

$$\frac{4}{3} \pi R^3 N < 1 \dots\dots\dots (3).$$

The concentration outside the films, as will be seen in the sequel, is practically the average concentration of the liquid. If, therefore, the particles are far apart, we shall by always assuming the permanent flow to take place, corresponding to a very (infinitely) thick layer, on the outside of which the average concentration of the liquid is maintained, obtain values for reaction velocity, which may be taken to be those belonging to the minimum conceivable amount of convection.

Deduction of a Formula for the Reaction Velocity Corresponding to a Minimum Amount of Convection.—We have to deal with the following case:—A sphere of given radius r is immersed in a solution of the concentration C_0 . On its surface the concentration is kept continually at zero, and at a distance R from its centre the concentration D is always to be found, which is not exceeded in any part of the liquid. The smallest conceivable amount of solute, Fdt , that could under these conditions flow to the sphere in the time dt , is the value which Fdt would have if the conditions we have assumed had already been in operation for an infinite period of time. This would mean that a permanent state had been established, and as it is our object to find a minimum value for the substance removed, the first part of our problem consists in determining Fdt corresponding to the permanent state.

The total amount of solute $F_{(x)}dt$ flowing in the time dt towards the centre of the sphere across a concentric spherical surface of radius x is given by

$$F_{(x)}dt = 4\pi\kappa x^2 \frac{\partial c}{\partial x} dt \dots\dots\dots (4),$$

if κ indicates the diffusion coefficient of the solute, and c its concentration at the points under consideration. From this equation we arrive by considerations of a well-known kind* at the relation

$$\frac{\partial c}{\partial t} = \kappa \left(\frac{\partial^2 c}{\partial x^2} + \frac{2}{x} \frac{\partial c}{\partial x} \right) \dots\dots\dots (5).$$

For the permanent state we have $\partial c / \partial t = 0$, the limiting conditions being

$$c = 0 \quad \text{for} \quad x = r \dots\dots\dots (6),$$

$$c = D \quad \text{for} \quad x = R \dots\dots\dots (7).$$

The result of the integration under these conditions is

$$c = D \frac{R}{R-r} \frac{x-r}{x} \dots\dots\dots (8),$$

and the amount removed at the surface of the small sphere in the time dt follows from Equation 4

$$Fdt = 4\pi\kappa r \gamma Ddt \dots\dots\dots (9),$$

the quantity γ being defined by

$$\gamma = \frac{R}{R-r} \dots\dots\dots (10),$$

and decreasing from infinity to 1 as R increases from r to infinity.

We now have to show that in all the cases we are dealing with the quantity D does not differ appreciably from the average concentration C of the liquid. Indicating again by N the number of particles per unit volume of solution, and by v their total volume, then

$$\frac{4}{3}\pi r^3 N = v \dots\dots\dots (11),$$

and C , which is equal to the total amount of solute per unit volume of liquid, is given by

$$C = N \int_r^R 4\pi x^2 c dx + (1 - N \frac{4}{3}\pi R^3) D.$$

Eliminating c and N from this expression by means of Equations 8 and 11 and simplifying, we obtain

$$C = D \left\{ 1 - \frac{1}{2} v \left[\left(\frac{R}{r} \right)^2 + \frac{R}{r} \right] \right\}.$$

* See e.g., Fourier's "Analytical Theory of Heat," §§ 112 and 113.

This equation, taken in conjunction with the inequality 3, and with Equation 11, leads to the conclusion that the greatest conceivable value for the difference between C and D is $\frac{1}{2}D (v^{\frac{1}{3}} + v^{\frac{2}{3}})$.

Now, in all the cases we have to consider v is smaller than 10^{-6} , so that we may, without appreciable error, make D equal to C. Remembering, also, that the decrease $-dC$ of C in the time dt equals $NFdt$, and expressing the radii of the spheres by their diameter L, we obtain from Equations 9 and 11

$$-dC = \frac{12\kappa v}{L^2} \gamma C dt,$$

from which, by utilising the limiting condition $C = C_0$ for $t = 0$, we find by integration

$$\frac{1}{t} \log \frac{C_0}{C} = K \dots\dots\dots (12),$$

the constant K being given by the equation

$$K = \frac{12\kappa v}{L^2} \gamma \dots\dots\dots (13),$$

and having the minimum value

$$K = \frac{12\kappa v}{L^2} \dots\dots\dots (14).$$

Examples to Show that Equations 9, 12, and 14, are a Close Approximation to the Correct Result.

(a) *A Sphere in Infinite Space.*—In deducing the foregoing equations, we assumed the permanent state to be always produced instantaneously, and we have made it clear that the result thus obtained for the rate of change of concentration will certainly not be too large. In reality, when the spheres are so small as those we have to deal with, and the volume they draw solute from more than a millionfold as great as their own, no appreciable error is made by our assumption. We can readily prove this by integrating Equation 5 completely for simple cases, and showing that the results approximate very quickly to those we have calculated.

As a first example, we determine the amount of solute which would be removed by each sphere after the time t if it were placed in an infinite amount of solution at the beginning of the experiment. For this purpose we calculate an expression for the concentration throughout the liquid at any time t by integrating Equation 5 under the limiting condition $c = D$ between $x = r$ and $x = \infty$ for $t = 0$, and the condition expressed by Equation 6.

The integral obtained is

$$c = D - \frac{Dr}{x} + \frac{2Dr}{\sqrt{\pi x}} \int_0^{\frac{x-r}{2\sqrt{\kappa t}}} dq e^{-q^2},$$

a result which can be verified without difficulty.

The amount of solute S removed by the sphere after the first t seconds is

$$\begin{aligned} S &= 4\pi\kappa r^2 \int_0^t \frac{\partial c}{\partial x} dt \text{ when } x = r \\ &= 4\pi\kappa Dr t + 8\sqrt{\pi\kappa t} r^2 D \end{aligned}$$

The first member on the right side of this equation is identical with the value which follows for R equal infinity from the Equation 9 we previously employed. Making $2r = 5 \times 10^{-5}$ cm, $R = 10^{-5}$ cm²/sec., we can calculate that the difference between this quantity and S amounts to only 0.9 per cent. of S after 1 second.

(b) *A Sphere in a Large Enclosed Spherical Space.*—The close approximation of the result expressed by Equations 12 and 14 to the correct value for stationary liquids, in which the radius of action of each spherical particle is great compared with its own diameter, is specially made clear by the full calculation of the case in which one of the spherical particles is placed in the centre of a spherical vessel of large diameter filled with solute. In this case we have to integrate Equation 5, the limiting conditions being firstly that no solute can pass through the wall of the vessel. Indicating the radius of the latter by R , this means that

$$F_R = 0, \text{ i.e., according to Equation 4, that } \frac{\partial c}{\partial x} = 0, \text{ for } x = R.$$

We have besides the limiting condition expressed by Equation 6 and the condition

$$c = C_0 \text{ between } x = r \text{ and } x = R, \text{ for } t = 0.$$

The differential equation can be integrated subject to these limits by methods similar to those employed in §§ 283 to 293 of Fourier's *Analytical Theory of Heat* for the determination of changes of temperature in a solid sphere. The following result is thus obtained:—

$$c = \frac{1}{x} [a_1 e^{-\kappa n_1^2 t} \sin n_1 (x-r) + a_2 e^{-\kappa n_2^2 t} \sin n_2 (x-r) + \dots],$$

the numbers n being determined as the successive roots of the equation

$$\frac{\tan n (R-r)}{nR} = 1,$$

and the coefficients a by the equation

$$a_p = C_0 \frac{\int_r^R x \sin n_p (x-r) dx}{\int_r^R \sin^2 n_p (x-r) dx} = C_0 \frac{1}{n_p} \frac{\frac{1}{2} \sin n_p (R-r) - R \cos n_p (R-r) + r}{\frac{1}{2} (R-r) - \frac{1}{4n_p} \sin 2n_p (R-r)}$$

This system of equations is simplified, and the dimensions of the quantities occurring in them made clear by introducing in place of a and n the quantities α and ν defined by the relations:

$$n(R-r) = \nu \quad \text{and} \quad a_p/n_p = \alpha_p C_0 (R-r)^2.$$

These quantities α and ν are functions only of the non-dimensional number ϵ defined by the equation

$$\epsilon = \frac{r}{R-r}.$$

After several transformations the final system of equations is arrived at.

$$C = \frac{C_0 (R-r)}{x} \left[\alpha_1 \nu_1 e^{-\kappa t \frac{\nu_1^2}{(R-r)^2}} \sin \nu_1 \frac{x-r}{R-r} + \alpha_2 \nu_2 e^{-\kappa t \frac{\nu_2^2}{(R-r)^2}} \sin \nu_2 \frac{x-r}{R-r} + \dots \right] \quad (15),$$

the quantities ν being found as the successive roots of the equation

$$\frac{\tan \nu}{\nu} = 1 + \epsilon \quad (16),$$

and the quantities α by the equation

$$\alpha_p = \frac{2\epsilon}{\nu_p^2 [1 - (1 + \epsilon) \cos^2 \nu_p]} \quad (17).$$

Values of time always exist for which the infinite series can practically be replaced by its first member. If ϵ be small the values for ν_1^2 and α_1 arising out of Equations 16 and 17 may be taken as

$$\nu_1^2 = 3\epsilon, \quad \alpha_1 = \frac{1}{3\epsilon},$$

and the whole expression simplified to

$$C = C_0 \frac{x-r}{x} e^{-12\kappa t \epsilon^3/L^2}.$$

The concentration varies with distance from the small sphere in the identical manner we found previously in Equation 8, and we have already proved that this being so the average concentration C may without appreciable error be assumed to be equal to the upper conceivable limit of c . We thus have

$$C = C_0 e^{-12\kappa t \epsilon^3/L^2},$$

an equation which by a slight transformation becomes identical with Equations 12 and 14.

The Application of Equation 14 to Bredig's Results Shows that they contradict Nernst's Hypothesis.—Equation No. 12 is identical in form with No. 1 which Bredig found to represent his experimental results. As the constant K is a measure for reaction velocities under corresponding conditions (see Equation 2), we can submit Nernst's hypothesis to the test we have outlined above by a comparison of the theoretical minimum value for K of Equation 14 with the experimental values found by Bredig.

We employ the results given by him in Table 7 'Zeitschrift f. Physikalische Chemie,' vol. 31, p. 285. The concentration of the platinum was here 31500^{-1} g-atom of platinum per litre, which is approximately 3150000^{-1} c.c. of platinum per c.c. We thus have to substitute $\kappa = 10^{-5}$ cm²/sec, $L = 5 \times 10^{-5}$ cm, and $v = 3150000^{-1}$ into Equation 14, and find

$$K = \frac{12 \times 10^{-5}}{(5 \times 10^{-5})^2 \times 3150000} = 0.0152 \text{ sec.}^{-1} = 0.91 \text{ min.}^{-1}.$$

Whereas the average value of Bredig's experiments in which $\frac{N}{2000} \text{ Na}_2\text{HPO}_4$ was present amounted to only $\frac{0.016}{0.4343} = 0.037 \text{ min.}^{-1}$, that is about one twenty-fifth of the calculated minimum number, and the average value in a solution containing no electrolyte whatever was $\frac{0.024}{0.4343} = 0.055 \text{ min.}^{-1}$, that is about one-sixteenth of the calculated value.

Even in alkaline solution in which the reaction proceeds very much faster, the velocity is smaller than the calculated value, whereas on Nernst's hypothesis it ought, as already explained, to be much greater. We employ the numbers given by Bredig in Table 12, p. 297, for a $\frac{N}{32} \text{ NaOH}$ solution, which probably correspond to the very greatest velocity measured by him. Here we have $v = 300000^{-1}$ g-atom of platinum per litre, that is approximately $v = 30000000^{-1}$ c.c. per c.c., the other quantities being the same as above. By Equation 14 we thus calculate

$$K = 0.0016 \text{ sec.}^{-1} = 0.096 \text{ min.}^{-1},$$

whereas the average value of the constant given by Bredig amounts to $\frac{0.0205}{0.4343} = 0.0472 \text{ min.}^{-1}$, that is about half of the calculated minimum value. We thus see that Bredig's reactions proceed far too slowly to allow us to reconcile them with Nernst's hypothesis.

An Equation of the Form of No. 1 expresses the Result if the Velocity of the Reaction Occurring on the Surface of the Particles is Proportional to the Concentration of the Solution in Immediate Contact with them.—The fact that the law obeyed by Bredig's reactions differs only in

the magnitude of a constant from the formula we have deduced on Nernst's hypothesis might, perhaps, seem an argument in favour of the latter.

We now proceed to show that we can obtain an equation of the same form as Nos. 1 and 12, but differing from Nos. 13 and 14 in the value of the constant K, if we drop altogether the assumption that equilibrium is permanently maintained on the boundary between the particles and the solution, *i.e.*, that the concentration of the hydrogen-peroxide is permanently maintained at zero. Instead we assume that the amount Fdt acted upon in the time dt by each particle is proportional to the concentration C' of the solute actually in contact with it. Retaining the same notation we employed above, we thus have

$$Fdt = \alpha 4\pi r^2 C' dt \dots\dots\dots (18),$$

α being a constant. The amount of substance removed on the surface of the particle must be replaced by diffusion from the interior of the solution as a discontinuity of concentration would otherwise occur. It can be expressed in terms of κ , γ and $D - C'$ by making use of Equation 9. This Equation was deduced on the assumption that the concentration on the surface of the particles is zero. As absolute values of concentration do not occur in Fick's law of diffusion, it is evident that we may generalise the result so as to comprise the case that the concentration on the surface of the particles is C' by replacing D of Equation 9 by the difference $D - C'$. We thus obtain

$$Fdt = 4\pi\kappa r\gamma (D - C') dt \dots\dots\dots (19)$$

Eliminating C' from Equations 18 and 19, we find

$$Fdt = \frac{4\pi\alpha\kappa r^2\gamma D}{\alpha r + \kappa\gamma} dt,$$

from which we deduce a formula identical with No. 12, by reasoning exactly analogous to that employed to establish it. The constant K in the present case, however, has the value

$$K = \frac{12\alpha\kappa\gamma v}{L(\alpha L + 2\kappa\gamma)},$$

the number γ varying according to the amount of convection from 1 to infinity, as is clear from Equation 10, and the number α having any positive value, which may be called the velocity constant proper of the reaction.

Thermodynamical Criticism of Nernst's Hypothesis.—In conclusion, it may be useful to criticise the principle put forward by Nernst from a thermodynamical point of view. The essence of it is contained in the following two sentences:—"Many facts lead to the assumption that equilibrium is established on the boundary of two phases, with

extremely great velocity. Such a behaviour is also, it seems, theoretically necessary, for, otherwise, finite differences of chemical potential would occur on the boundary of two phases, *i.e.*, at infinitely near points, which would manifestly lead to infinitely great forces and reaction velocities."

As is well known, we owe Nernst the calculation of the diffusion coefficient of an electrolyte, which probably forms the most brilliant instance we possess for the deduction of the velocity of a natural process from thermodynamical data. In this case, the force is calculated which may be considered to act upon a g-ion of electrolyte (force due to osmotic pressure) in a solution of uneven concentration, and by assuming the mobility of the ions to be the same, whether under the influence of forces due to difference of concentration, or under that of electric forces, the diffusion coefficient of the electrolyte can be calculated. Here we have an instance to which the considerations quoted above from Nernst apply beyond doubt. We may put the matter in the following form:—If a discontinuity of concentration were to occur in a solution, we should have finite differences of thermodynamical potential at infinitely near points, or, in other words, finite amounts of work would become available in order to move a given quantity of solute an infinitely small, or, at least, a very small way. Now, as the work required to overcome internal resistance in moving a finite quantity of solute through an infinitely small stretch of solution is infinitely small, a condition such as the one considered would lead to an infinite flow of solute. Similarly, if a solid be brought together with its unsaturated solution, finite amounts of free energy are available to dissolve a given quantity. Now, in this case, although it is not *a priori* certain, yet it is exceedingly probable that the work is practically infinitely small which is necessary to overcome internal resistance in transferring substance an infinitely small distance from the solid to the liquid phase. We may, therefore, conclude that a practically infinite instantaneous flow would occur, and bring about equilibrium on the boundary. Similar considerations probably apply to most physical processes, or, at any rate, to such as are capable under any conditions of occurring in a reversible manner.

When, however, we turn to chemical processes, we meet with a difference in principle. If we wish to consider a chemical reaction as a transference of atoms over molecular distances, we can no longer say that the work in overcoming internal friction during this transference is a negligible quantity for a finite amount of substance. If it were, it is evident that all chemical reactions in homogeneous systems during which finite amounts of free energy are destroyed, should be instantaneous. This is, however, not the case. In fact, it is not clear why a chemical reaction should proceed with greater velocity on the boundary of two phases than in the interior of one of them. It is not

to be denied that many chemical reactions do take place instantaneously on the boundary of two phases, and a considerable number of interesting cases have been investigated by Brunner,* which evidently conform to this rule. It does not, however, seem probable that a useful purpose would be served in considering this rule to hold universally.

I have examined consequences drawn from it with regard to irreversible electrolytic reductions, and do not find them to agree with facts.† Many other cases might also be brought forward that would be very difficult to reconcile with this theory, *e.g.*, the great difference of velocity shown by metals in dissolving in different acids,‡ catalysis by substances such as nitrogen peroxide during the solution of copper in nitric acid, and others.

In conclusion, the author desires to say that he has had the advantage of discussing the matter treated in this paper with Dr. Senter and Professor Poynting, for which he acknowledges his indebtedness.

“On Galvanic Cells produced by the Action of Light. Preliminary Communication.”§ By M. WILDERMAN, Ph.D., B.Sc. (Oxon). Communicated by Dr. LUDWIG MOND, F.R.S. Received November 8,—Read November 24, 1904.

(From the Davy-Faraday Laboratory of the Royal Institution.)

In my paper “On Chemical Statics and Dynamics” (‘Phil. Trans.,’ A, vol. 199, 1902, p. 337), and especially ‘Zeit. Physik. Chemie,’ vol. 42, 1902, pp. 316—335, I deduced, from thermodynamics, the laws experimentally found by me for velocity of chemical reaction, and for chemical equilibrium under the action of light, from the fundamental conception that the chemical potential of substance in light and in the dark is different, becoming greater in light. The foundation for this conception was that two metallic plates immersed in a liquid and connected to a circuit form a “galvanic” combination, when one plate is exposed to light while the other is kept in the dark; and, according to Gibbs’ equation, $v'' - v' = \alpha_a(\mu_a' - \mu_a'')$, no galvanic cell could be formed, unless the chemical potentials at the two electrodes were different in light and in the dark.

The experiments of Becquerel and Minchin left students to infer

* ‘Ztschft. Phys. Chem.,’ vol. 47, p. 56 (1904).

† Faraday Society, October 25, 1904.

‡ Ostwald, ‘Grundlinien d. anorganischen Chemie,’ p. 249.

§ This paper contains a preliminary account of the author’s further researches on “Chemical Statics and Dynamics of Reversible and Irreversible Systems under the Action of Light.”